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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM (II) WITH RUBEANIC ACID (RA) IN PRESENCE OF PYRIDINE, PIPERIDINE AND 3-PICOLINE

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Unpretentious and exclusive methods for the spectrophotometric determination of trace amount of divalent palladium (II) have been developed with rubeanic acid (dithio-oxamide) in presence of secondary ligands like pyridine, piperidine and 3-picoline. Both direct and extraction spectrophotometry showed that coloured rubeanates are only stable in acidic medium. The violent yellow coloured products are formed below pH 5.0 with an absorption maxima at 416.0 and 422.0 (pyridine), 405.0 and 416.5 (piperidine) and 418.0 and 422.0 (3-picoline) both in direct and isoamyl alcohol (IAA) extracted system, respectively. Results indicate that the highest sensitivity and molar absorptivity of Pd-RA pyridine system in direct spectrophotometry were 0.01497 μg Pd (II) cm^{-2} and 7107.89 L mol^{-1} cm^{-1} respectively. IAA extracted Pd-RA-piperidine system was found to give a sensitivity of 0.01087 μg(Pd(II) cm^{-2} and molar absorptivity of 9788.80 L mol^{-1} cm^{-1} which were the highest of all the system. The effects due to variation of pH, reagent concentrations, order of addition of reagents, time, temperature and solvent media on the absorption spectra have been investigated and the optimum conditions determined. The effects of diverse ions and their tolerance limit have also been studied.

Key words : Spectrophotometry, Rubeanic acid, Secondary ligands, Palladium (II).

Introduction

Of the various organic ligands which have been found to act as excellent chelating agents, rubeanic acid constitutes a very important class, (Ray and Xavier is 1961) and is extensively used as analytical reagent for the determination of various metals *(*Saha and Chakraburtty 1983 2&3; *Bozhkov et al 1988).* There exists scanty informaton about the techniques for the determination of trace amount of palladium. Bobtelsky and Eisenstadter (1957) reported that palladium combines with rubeanic acid to give a number of compounds having the composition Pd_3RA_2, PdRA, Pd_2RA_3, and $PdRA_2$ (where RA= rubeanic acid molecule or its radical), depending on the pH of the medium during precipitation and the amount of reagent present. But methods have not been developed for spectrophotometric determination of Pd(II) with rubeanic acid in presence of various secondary ligands. In this paper a systematic study has been presented for establishing a spectrophotometric method for the determination of palladium with rubeanic acid. Secondary ligands have also been employed, because the solubility of Pd(II) complex with rubeanic acid and aromatic heterocyclic bases makes a suitable ligand pair for determination of trace amount of Pd(II) spectrophotometrically.

Effects of pH, reagent concentrations, order of addition of reagents, time, temperature, diverse ions etc. and the applicability of the Beer's Law for both direct and isoamyl alcohol extraction spectrophotometry were also studied.

Experimental

Stock Solution of Pd(II). A stock solution of palladium (200 of μg ml^{-1} or 0.2 mg cm^{-3}) (E. Merck) was prepared by dissolving the analytical grade palladium chloride in deionized water with the aid of 0.01 N HCl and standardized (Vogel, 1989).

Reagent and secondary ligands solutions. A 0.1% solution of rubeanic acid (RA) (E.Merck) was prepared in 95% ethyl alcohol. A 10% (v/v) alcoholic solutions of the purified bases (reagent grade) were used.

Buffer solutions: Buffer solutions of titrisol (E. Merck) having different pH were used.

Solvent : Isoamyl alcohol (E.Merck) was used for extraction.

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Solution of foreign ions : The solutions of foreign ions were prepared from reagent grade salts.

Apparatus : Absorbance measurements were carried out with a Shimadzu model UV-160A, UV-Visible double beam recording spectrophotometer employing a matched pair of 1 sq. cm fused silica absorption cells. A Hanna digital pH meter with recorder was used for pH measurement. Pear shaped 50 ml separatory funnels with short stems were used for the extraction work.

General Procedure for Direct Spectrophotometry : In a 25 ml beaker, palladium chloride solution containing between 5 to 200 μg Pd(II), 1.0 ml of buffer solution of desired pH and 0.75 ml of rubeanic acid were introduced one after another followed by addition of 0.2 ml of the base solution. The mixture was transferred into a 10.0 ml volumetric flask and the volume made up to the mark with ethyl alcohol (Analar grade) and final pH was measured. After 3 min, the absorbance of each of the resulting solutions was measured at the respective absorption maxima λ_{max} against reagent blank.

General Procedure for extraction Spectrophotometry : 5 to 150 μg (Pd(II) from palladium chloride stock solution was transferred into a 50 ml separatory funnel followed by the addition of 1.0 ml of buffer solution of desired pH and 0.75 ml of rubeanic acid. The mixture was then shaken for a minute, measured volume (5 ml) of IAA was then added and the resulting mixture was shaken for another 2-3 min for the preliminary separation of the two phases and then 0.3 ml of base solution was added to the system. The resulting mixture was again shaken vigorously for about 5 min and the yellow coloured organic layer was allowed to separate which was drained out and dried over anhydrous sodium sulphate to remove the moisture. To ensure complete recovery of Pd(II), the aqueous layer was extracted twice with 2 ml portion of IAA. The combined extract, after removing the moisture was transferred into a 10 ml volumetric flask. Finally, the extract was diluted to 10 ml with IAA. A reagent blank was prepared under identical conditions against which the absorbance of coloured product was measured at the respective absorption maxima.

Results and Disucssion

Preliminary investigations showed that palladium (II) reacted with rubeanic acid and developed an intense yellow color. The intensity of the color increased up to pH 5.0 then decreased. Addition of different bases enhanced this colour development. Rubeanic acid in conjunction with pyridine, piperidine and 3-picoline formed stable and soluble intense coloured complexes with palladium (II) at an optimum pH which showed an absorption maxima for individual systems where Beer's Law was obeyed. The organic solvents like chloroform, carbontetrachlolride, methyl isobutyl ketone (MIBK) and isobutyl alcohol (IAA) were examined as extractants. IAA was found to be the most favourable. All the bases were examined for synergistic extraction of Pd (II)-RA complex under the present conditions of investigation. It was observed that extraction could be performed completely with definite synergistic effect while for direct spectrophotometry, the presence of the bases had little synergistic effect on the system. Spectral characteristics of Pd(II)-RA complexes in presence of different bases for both in direct spectrophotometry and in their IAA extracts are shown in Tables 2 and 3 respectively.

Absorption spectra. Figures 1 and 2 represent the absorption spectra of Palladium (II)-RA in presence of pyridine, piperidine and 3-picoline for direct and extraction spectrophotometry, respectively. All subsequent measurements were carried out at their respective absorption maxima.

Table 1

Spectral characteristics of Pd(II) - rubeanic acid complexes in presence of different organic bases.

Bases	Optimum pH	Absorption Maxima nm	Molar absorptivity $Lmol^{-1} cm^{-1}$	Sensitivity $\mu g\ cm^{-2}$	Beer's Law [optimum concentration of Pd(II)] range,ppm	Photometric error (%)	Standard deviation (Relative standard deviation)
Pyridine	1.80	416.0	7107.89	0.01497	4.5-13.0 (4.5-11.7)	2.72	$\pm 0.5676 \times 10^{-3}$ (0.1700%)
Piperidine	2.75	405.0	6448.18	0.0165	3.0-14.0 (3.6-12.1)	2.72	$\pm 0.7379 \times 10^{-3}$ (0.249%)
3-picoline	1.75	418.0	6341.77	0.01678	3.0-14.5 (3.0-11.5)	2.72	$\pm 0.9428 \times 10^{-3}$ (0.3164%)

Table 2

Spectral characteristics of IAA extracted Pd(II)-rubeanic acid complexes in presence of different organic bases.

Bases	Optimum pH	Absorption Maxima nm	Molar absorptivity $Lmol^{-1} cm^{-1}$	Sensitivity $\mu g\ cm^{-2}$	Beer's Law [optimum concentration of Pd(II)] range,ppm	Photometric error (%)	Standard deviation (Relative standard deviation)
Pyridine	2.90	422.0	8866.67	0.01200	2.5-10.5 (3.1-8.2)	2.72	$\pm 0.8498 \times 10^{-3}$ (0.3392%)
Piperidine	3.0	416.5	9788.80	0.01087	2.0-10.0 (2.8-9.2)	2.72	$\pm 0.9189 \times 10^{-3}$ (0.3327%)
3-picoline	2.80	422.0	8866.67	0.01200	2.0-11.0 (3.2-10.2)	2.72	$\pm 0.9189 \times 10^{-3}$ (0.3679%)

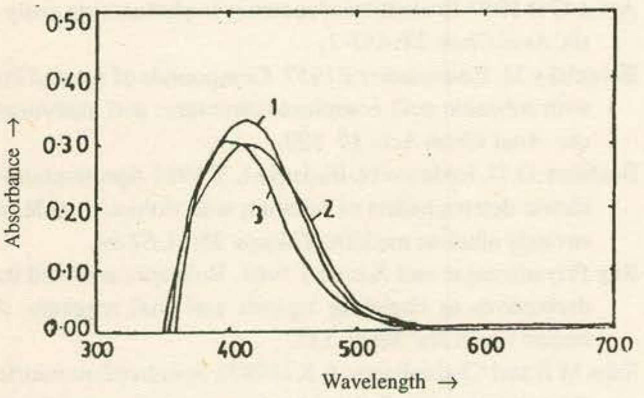

Fig 1 Absorption spectra of Pd (II)- Rubeanic acid complexes in presence of 1 pyridine 2. piperidine and 3.3-picoline at a pH of 1.80, 2.75 and 1.75 respectively. Palladium (II) concentration = 5 ppm.

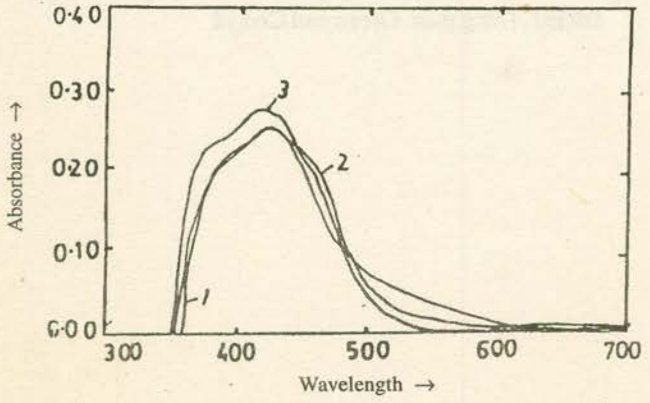

Fig 2 Absorption spectra of isoamylalcohol (IAA) extracted Pd (II)- Rubeanic acid complexes in presence of 1. pyridine 2. piperidine and 3.3-picoline at a pH of 2.90, 3.00 and 2.80 respectively.Palladium (II) concentration = 3 ppm.

Effect of pH, reagents, order of addition of reagents, time and temperature. For direct and extracted systems, the effect of pH was studied with 5 ppm and 3 ppm of Pd(II) solution. pH 1.80, 2.75 and 1.75 were found to be the optimum for systems containing pyridine, piperidine and 3-picoline for direct spectrophotometry. For the extraction spectrophotometry the optimum pH values were 2.90, 3.00 and 2.80 for system containing pyridine, piperidine and 3-picoline. The rubeanic acid of 0.5, 0.75 and 0.3ml were found to be sufficient for 5 ppm and 3 ppm of Pd(II) during direct and extraction spectrophotometry for pyridine, piperidine and 3-picoline respectively. The excess of the reagent had no effective influence on the determination of Pd(II).

0.2 ml of 10% alcoholic solution of bases was found to be adequate for maximum colour development for all the systems, investigated and excess of the base actually decreased the colour due to the change in pH of the systems. Changes in order of addition of the reagents did not affect the development of full color. Usually it was necessary to add buffer solution to metal (salt solution) before the addition of rubeanic acid and other reagents. The colour in Pd(II)-RA systems in alcoholic medium developed within a minute and was stable for about 2-3 h and the color intensities in extracted systems were found to be stable for 5-6 h. The colour intensity was unaffected by variation in temperture for both the systems from 20-40°C.

Beer's law and optimum concentration range. Beer's Law range and the corresponding optimum working range as obtained from plot (Table 1 and 2) indicate that the presence of pyridine in both the alcoholic medium and extracted system had the shortest concentration range of palladium (II) adhering to Beer's Law while the presence of 3-picoline gave the

Table 3

Estimation of trace amount of palladium (II)

Sample No.	*palladium taken (mg)	Spectrophotometric estimation of palladium in mg	Error %
1	0.059	0.058	+1.69
2	0.065	0.066	-1.54
3	0.124	0.122	+1.61

* Estimated by standard method (Vogel 1989).

largest concentration range for both direct and extraction spectrophotometry.

Molar Absorptivity and Sensitivity : The results of molar absorptivity and sensitivity are shown in Table 1 and 2. It is observed that Sandell's (1959) sensitivity and molar absorptivity of the mixed ligand complexes of Pd(II) are much more higher in extracted systems.

Photometric Error and Precision : The relative errors per 1% absolute photometric error calculated from Ayres (1949) equation, are shown in Table 1 and 2 for both the direct and IAA extracted spectrophotometry. The photometric error (2.72%) is observed to be the same for all the systems investigated. The precision of the methods was studied by analyzing ten solutions for each case. The mean absorbance, standard deviation and relative standard deviation revealed that the methods are precise and give reproducible results.

Effect of diverse ions : Palladium (II) (5 ppm) could be estimated within an error of ±2% in presence of the following ions of concentrations shown in the parentheses in ppm.

Co^{+2} (125), Fe^{+2}(6), Fe^{+3}(8), UO_2^{+2}(15), Ni^{+2} (200), Mg^{+2}(115), Ca^{+2}(200), Ba^{+2}(250), Hg^{+2} (35), Ag^{+2}(75), Cu^{+2}(60), Sb^{+3}(150), Sr^{+2} (110), NH_4^{+} (250), Al^{+3} (125), Cd^{+2} (200), Sn^{+2} (80), Sn^{+4}(125), Zn^{+2}(135), VO_4^{+3}(10), Acetate (75), Borate (50), Phosphate (35)

Oxalate interfere seriously owing to the complex formation with palladium (II).

Analytical applications : With a view to evaluate the applicability of the spectrophotometric method [Pd(II)-RA-piperidine IAA extracted system] for determination of trace amount of Pd(II), an attempt was made to apply it to the simulated test samples. The concentration of palladium (II) in the test sample was determined by standard method (Vogel 1989) and then the Pd(II)-RA-piperidine (IAA extracted) spectrophotometric method was applied for estimation of palladium. Results revealed that the method developed is suitable for the estimation of trace amount of palladium Table 3.

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